



Titanium dioxide photocatalytic decomposition of ethyl-S-dimethylaminoethyl methylphosphonothiolate (VX) in aqueous phase

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ABSTRACT

The TiO₂ photocatalytic decomposition of ethyl-S-dimethylaminoethyl methylphosphonothiolate (VX) as a real chemical warfare agent (CWA) in liquid phase has been investigated by gas chromatography/mass spectrometry (GC/MS) and liquid chromatography–tandem mass spectrometry (LC–MS/MS) analysis. The TiO₂ photocatalytic decomposition rate, r_{VX} , was accelerated with increase in alkalinity. The several kinds of by-products such as diisopropylamine, ethyl methylphosphonic acid, oxygenated VX and partially oxidized VX were observed. On the basis of the by-products, the TiO₂ photocatalysis were proposed as the P–S, C–N cleavage and oxygenation of VX molecule carried out mainly. The difference between r_{VX} and vaporized dimethyl methylphosphonate (DMMP), r_{DMMP} as CWA simulant was also investigated and the r_{VX} was 30 times faster than the r_{DMMP} . On the basis of the decomposition mechanism of VX and DMMP molecules, the results of the acceleration of r_{VX} in alkaline condition and of the comparison of r_{VX} and r_{DMMP} were also discussed.

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1. Introduction

Decontamination of the environmental area contaminated by chemical warfare agents, CWAs, has been studied [1–6]. Since titanium dioxide (TiO₂) has been shown to be an effective photocatalyst for the decomposition of a large number of organic compounds, use of TiO₂ as a photocatalyst has been greatly focused on the decontamination of the CWAs in terms of crisis management [7–13], and hence a lot of studies using CWA simulants have been carried out in the gas and liquid phase. Dimethyl methylphosphonate (DMMP) has been known for one of the major simulants as a nerve agent, which is isopropyl methylphosphonofluoridate, sarin (GB) and trimethylpropyl methylphosphonofluoridate, tabun (GA) and ethyl-S-dimethylaminoethyl methylphosphonothiolate (VX) as shown in Scheme 1 [14–29]. 2-(Butylamino)ethanethiol (BAET) has also been used as VX simulant on TiO₂ photocatalysis study [30]. Although a number of studies using CWA simulants have examined the reaction of gas and liquid phase, a few studies on the photocatalytic decomposition for CWAs have been reported. Recently, the

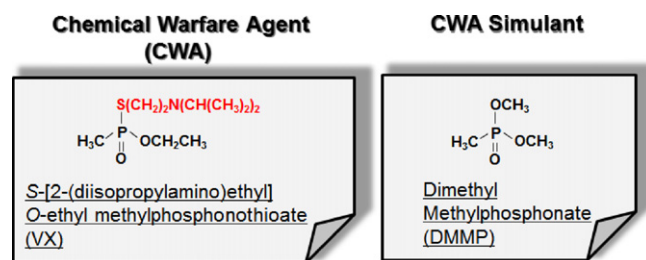
photocatalytic adsorption and decomposition mechanism for GB as a real CWA by ATR–FTIR technique and GC–MS analysis has been reported, and the complete decomposition has been demonstrated by our research group [31,32].

Among the nerve agents in CWAs, VX molecule is very stable in aqueous and gas phase, even at the surface of metal oxide powder [33–49]. The VX molecule is gradually decomposed in these conditions. Then EA2192 as a strongly toxic intermediate molecule is produced in aqueous phase and the lifetime of EA2192 is long [33–43]. A lot of research groups therefore have tried decomposing VX effectively by adding reagents, such as H₂O₂ solution and oxidant reagent, in aqueous phase [35,40]. However, few studies on the photocatalytic decomposition on the real VX have been reported, besides the comparison of VX and DMMP as a VX simulant in the TiO₂ photocatalysis has not also been reported yet.

Herein, we focus on the nerve agent VX as a real CWA in aqueous phase and report the results of the TiO₂ photocatalytic decomposition by GC–MS analysis. In the present paper, effect of pH, quantity of TiO₂ powder and concentration of VX molecules in the TiO₂ photocatalysis were mainly researched. The photocatalytic decomposition mechanism was then analyzed on LC–MS/MS. The differences in the photocatalytic decomposition of VX and DMMP are also examined (Table 1).

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Scheme 1. Molecular structure images of ethyl-S-dimethylaminoethyl methylphosphonothiolate (VX) and dimethyl methylphosphonate (DMMP).

2. Experimental

2.1. Samples

TiO₂ powder (P25, Japan aerogil) was used as a photocatalyst. The primary particle size, BET surface area and crystallinity of the P25 TiO₂ powder are 32 nm, 49 m²/g and 80% anatase–20% rutile mixture powder, respectively [50]. Ethyl-S-dimethylaminoethyl methylphosphonothiolate, VX, was obtained from TNO Prince Maurits Laboratory, Rijswijk, the Netherlands (the purity was >97% according to the supplier) and used with the permission of the Ministry of Economy, Trade and Industry of Japan. Dimethyl methylphosphonate (DMMP: Aldrich, >97%), H₃BO₃ (Wako, >99.5%), KCl (>99.5%, Wako), HCl (35–37%, Wako), NaOH (>97%, Wako), dichloromethane (DCM) (>99%, Wako) and ammonia solution (28%, Wako) were used without further purification.

2.2. Photocatalytic reaction

Typically, the TiO₂ powder was exposed to UV light (EFD 15 BLB, 15 W, Toshiba, center wavelength: 354 nm and the light intensity 6.3 mW/cm², TOPCON UVR-2(UD-36)) for 1 h under ambient air to remove surface pollutants. The TiO₂ powder was added in Milli-Q water and was agitated by sonication for 15 min. After agitation, pH of the TiO₂ suspension was adjusted with 0.1 M NaOH and HCl solution. As for the LC–MS/MS analysis, the pH of TiO₂ suspension was adjusted to 9 by adding ammonia solution. The TiO₂ suspension was finally injected in a vial. In this study, a Teflon cap was used for preventing VX adsorption at the cap.

Table 1
Characteristic physical and chemical properties of VX and DMMP.

	VX	DMMP
Vapor pressure: Log <i>P</i> (Torr)	^a 14–5200/ <i>T</i> (K)	^b 0.16–32.6/{ <i>T</i> (K) – 51.7}
p <i>K</i> _a	^c 8.6	^d 2.37
<i>E</i> _a in alkaline solution (kJ/mol)	^e 60.7 (P–S, P–O cleavage in alkaline > pH 12)	^f 52–62 (P–O cleavage)
	^g 107.5 (C–S cleavage)	
<i>E</i> _a at metal oxide (kJ/mol)	^h 46 (P–S cleavage) ^h 80 (P–O cleavage)	^h 49 (P–O cleavage)
Boiling point (°C)	^a 298	^d 181
Molecular weight	^a 267.4	^d 124.08
Melting point (°C)	^a –39	^d <50
Density (g/ml)	^a 1.0085 at 25 °C	^d 1.145 at 20 °C

^a Ref. [4].

^b Ref. [52].

^c Ref. [51].

^d Ref. [53].

^e Ref. [33].

^f Ref. [54].

^g Ref. [48].

^h Ref. [55].

Initial concentration of VX and DMMP reagents in the TiO₂ suspension was adjusted to be 1 μM. The vial was put on a seesaw shaker (Model-2230, Wakenyaku Co. Ltd.) to stir the TiO₂ suspension containing VX or DMMP. As a photocatalytic reactor, an aluminum box with UV light inside was covered the lid on the seesaw shaker. The shaker speed was set at 8 of the dial of the equipment. The DMMP or VX molecules in TiO₂ suspension of NaOH–HCl, ammonia and H₃BO₃–KCl–NaOH solution were stable in the dark. UV light irradiation was carried out with Black light (EFD BLB15W, center wavelength 352 nm, Toshiba) at a 10 mW/cm² light intensity at the surface of vial. All experiments were carried out in ambient.

2.3. GC/MS and LC–MS/MS analysis

Of the VX solution in TiO₂ suspension, 1 ml was drawn from the vial every 5 min under UV irradiation and 100 μl of DCM containing 2-amino-2-hydroxymethyl-1,3-piropenediol was added into the 1 ml of TiO₂ suspension to extract VX from the water phase. The suspension was then vigorously shaken with vibrator (Vortex-2 Genie) for several minutes. After stirring, the TiO₂ powder was removed by centrifuging at 3000 r.p.m. and the DCM phase was extracted from the centrifuged one.

The extracted DCM containing VX was analyzed on GC–MS chromatograph Agilent 6890 (MS: Agilent 5973 GERSTEL Modular Accelerated Column Heater). The concentration of the VX in DCM was calibrated by calibration experiment. The concentration of DMMP was also estimated from calibration curve by injecting the known concentration of DMMP.

After verifying complete decomposition of VX by GC–MS analysis, the TiO₂ suspension was centrifuged at 3000 r.p.m. to remove TiO₂ powder. Decomposition products of VX remaining in water phase was analyzed on LC–MS/MS (LC System: Paradigm MS4 (Michrom BioResources Inc., Auburn, CA), column: Atlantis T3 3 μm (2.1 i.d. × 100 mm) Waters, flow rate: 150 μl min^{–1}, mobile phase A: H₂O/MeCN/HCOOH = 98/2/0.1 (v/v/v), mobile phase B: H₂O/MeCN/HCOOH = 10/90/0.1 (v/v/v), binary gradient profile: 0–1 min 5% B; 1–10 min 5–95% B; 10–12 min 95% B. MS System: LTQ Orbitrap XL (Thermo Fisher Scientific), Capillary voltage: +5.0 kV, sheath gas flow rate: 30 arb. units, temperature of heated capillary: 275 °C, tube lens voltage: 70 V). In our study, negatively charged ionized compounds were observed. The pH 9 solution was then adjusted with ammonia solution to avoid analysis errors and damage of LC–MS/MS equipment. The LC–MS/MS analysis was limited only after the complete decomposition of VX molecular structure because it must not admit to handle the VX outside the special area of NRIPS.

Caution: VX as CWA used in these experiments is highly toxic by both inhalation and ingestion. The compound was always handled with special care in a special experimental room under reduced air pressure and should be immediately destroyed with sodium hypochlorite after use. Every experiment was performed by trained personnel and using applicable safety procedures in a special laboratory of NRIPS with the permission of the Ministry of Economy, Trade and Industry of Japan.

3. Results and discussion

3.1. pH dependence

As shown in Fig. 1(a), the concentration of VX, *C*_{VX}, was stable for 10 min in the dark and started decreasing with UV irradiation on each pH condition. The pH of solution was adjusted between 7 and 10 with 1 M NaOH and HCl. The quantity of TiO₂ was adjusted to be 1 g/l. The decrement of *C*_{VX} was accelerated with increasing alkalinity from 7 to 10. The photocatalytic decomposition rate, *r*_{VX},

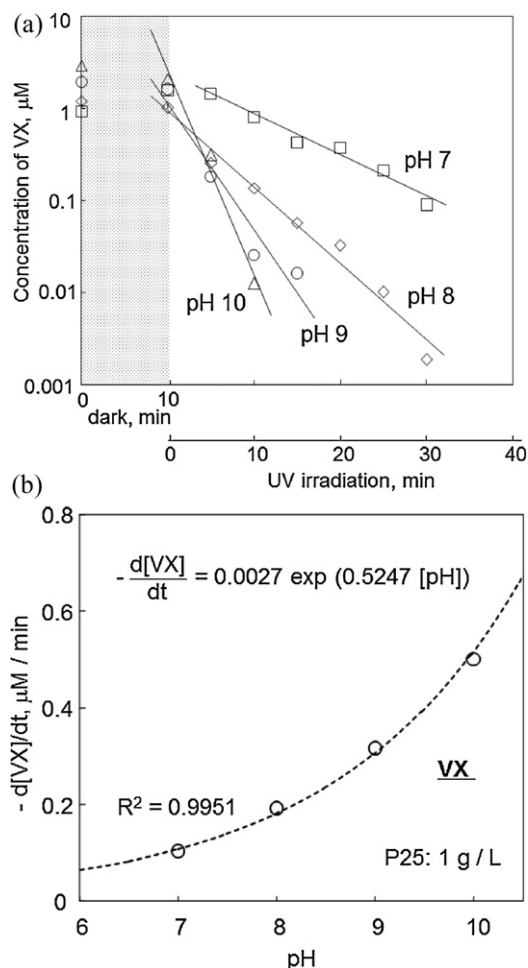


Fig. 1. (a) The pH dependence on TiO_2 photocatalytic decomposition of VX molecules. The pH was four different values from 7 to 10 adjusted by 0.1 M NaOH and 0.1 M HCl. (b) The r_{VX} was plotted as a function of the pH. The r_{VX} was calculated by first order kinetics equation from (a).

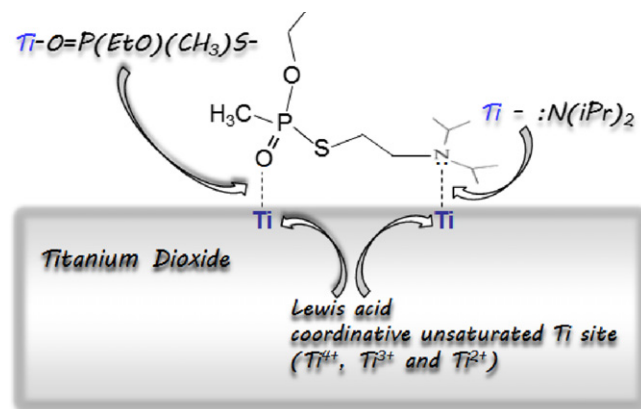
then obeyed first order reaction and the r_{VX} was plotted in Fig. 1(b) as a function of pH. On the basis of Fig. 1(b), alkaline condition is effective on the TiO_2 photocatalytic decomposition of VX molecule and the r_{VX} is significantly small below 6 of pH. The r_{VX} and its half-life time, $\tau_{0.5}$, are listed in Table 2.

The result of the acceleration of r_{VX} with increase in alkalinity was the same tendency as the pH dependency on the half-lifetime of VX in aqueous phase. The increase of the hydrolysis in the alkaline condition without the TiO_2 photocatalysts has been well known and is attributable to the increase in the concentration of OH^- to accelerate the self-hydrolysis of VX [33,34,36,51]. However, the fact

Table 2
pH dependence on rate constant and half-life time of VX molecules in TiO_2 photocatalysis.

pH dependency			TiO_2 quantity dependency		
pH	k (μM/min)	$t_{0.5}$ (min)	g/l	k (μM/min)	$t_{0.5}$ (min)
7	0.10	6.93	0.1	0.26	2.67
8	0.19	3.65	1	0.39	1.78
9	0.32	2.17	10	0.62	1.11
10	0.50	1.39			

The concentration of VX was 1 μM. In the case of pH dependence examination, the quantity of TiO_2 was adjusted to 1 g/l. The pH was then adjusted by 0.1 M NaOH and HCl solution. The pH in the TiO_2 quantity dependence examination was adjusted to 9 by H_3BO_3 –KCl–NaOH buffer solution.



Scheme 2. Plausible images of the adsorption structure of the VX molecules at the surface of TiO_2 speculated in this study.

that the C_{VX} was very stable in the dark for 10 min as seen in Fig. 1(a) indicates that the r_{VX} is exactly much faster than the self-hydrolysis rate in alkaline water only without TiO_2 photocatalysis.

In the case of the TiO_2 photocatalysis in aqueous phase, an adsorption of the VX molecule at the surface of TiO_2 may be effectively increased with increase in alkalinity. On the basis of the strong adsorption of the P=O group in the VX molecules adsorb at Lewis acid site at the coordinative unsaturated Ti site such as Ti^{4+} , Ti^{3+} and Ti^{2+} because the O=P group has a lone pair [14,16,17,20,21,31]. Here, the VX molecular structure in aqueous phase is controlled by pH because pK_a of VX at $N:H \leftrightarrow N: + H^+$ is at 8.6 [51]. It is then expected that the number of $N(iPr)_2$ group effectively increases with increase in alkalinity. The $N(iPr)_2$ group then can probably adsorb at the Ti site as a consequence of the lone pair. That is, the VX molecule adsorbs at the Ti site of the surface of TiO_2 by $Ti-O=P(EtO)(CH_3)S-$ and $Ti-N(iPr)_2$ bond formation as represented in Scheme 2 and the number of bond formation increases in alkaline condition. The formation of the $Ti-N(iPr)_2$ bond at the surface of TiO_2 accelerates the partial decomposition of the $N(iPr)_2$ group of the VX molecular structure. It suggests that the acceleration of r_{VX} with increase in the alkalinity is attributable to the increase of the partial decomposition of VX molecular structure.

As mentioned above, the alkaline condition above pK_a of VX is suitable for the TiO_2 photocatalysis to decompose VX molecule. Accordingly, the pH 9 was mainly used as suspension condition in this study and the solution at pH 9 was then adjusted with H_3BO_3 –KCl–NaOH buffer to avoid the pH change in the TiO_2 photocatalytic decomposition of VX molecules.

3.2. Quantity of TiO_2 powder dependence

Since the r_{VX} was affected by the quantity of TiO_2 powder, the TiO_2 suspension was adjusted to be three different quantities from 0.1 to 10 g/l as shown in Fig. 2(a). The C_{VX} was very stable at 1 g/l in the dark for 30 min, indicating that the VX molecule decomposition by hydrolysis was very slow in the TiO_2 suspension at pH 9 solution composed of H_3BO_3 –KCl–NaOH buffer. The C_{VX} in 0.1–10 g/l of TiO_2 suspension started decreasing with UV irradiation and the decrease of C_{VX} obeyed first order reaction. The r_{VX} of them was then plotted in Fig. 2(b) as a function of the quantity of TiO_2 powder. As shown in Fig. 2(b), the r_{VX} is accelerated with increase in the quantity of TiO_2 powder, which indicates that highly concentrated suspension is effective to decompose VX molecules in aqueous phase. However, the photocatalytic decomposition efficiency will be decreased at the highly concentrated suspension above 10 g/l as a consequence

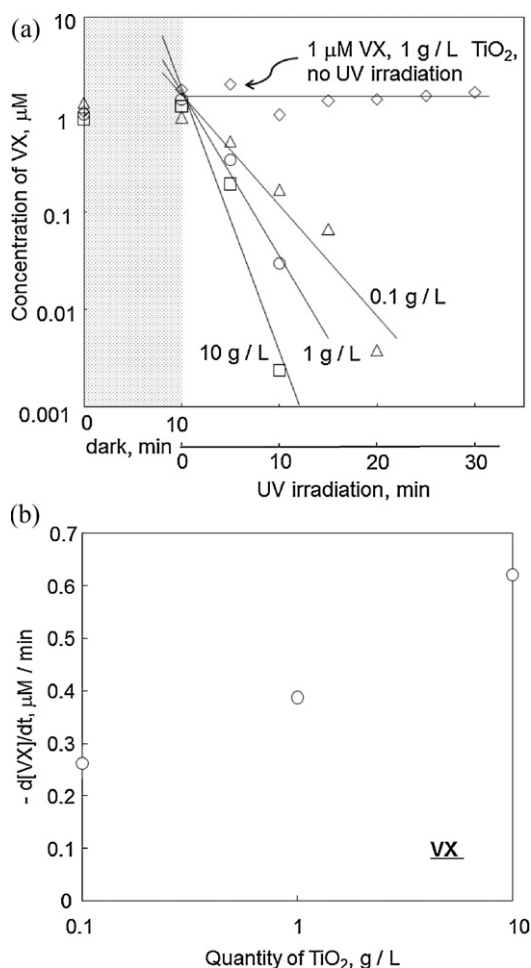


Fig. 2. (a) The quantity of TiO₂ dependence on the TiO₂ photocatalytic decomposition of VX molecules. The TiO₂ suspension was three different quantities from 0.1 to 10 g/L. The pH of suspension was adjusted to 9 with H₃BO₃–KCl–NaOH buffer. (b) The r_{VX} was plotted as a function of the quantity of TiO₂. The r_{VX} was calculated by first order kinetics equation from (a).

of inner filter effect by suspension itself. Of suspension, 1 g/l was accordingly employed as the concentration of TiO₂.

The r_{VX} at pH 9 of 1 g/l as seen in Figs. 1(b) and 2(b) was not controlled by pH control chemicals such as NaOH, HCl and H₃BO₃, it was suggesting that no TiO₂ photocatalysis to decompose VX was strongly controlled by pH control chemicals.

3.3. VX concentration dependence

The r_{VX} is strongly controlled by the initial C_{VX} , three different initial concentrations, 1, 3 and 10 μM were then employed. Fig. 3(a) shows the decrease of the C_{VX} in the TiO₂ photocatalysis. The C_{VX} was stable for 10 min in the dark and was gradually decreased with UV irradiation starting as to 1 μM VX. Induction period appeared at 3 μM C_{VX} and it remarkably appeared for 20 min at 10 μM. The induction period is zero order reaction contributing to the surface reaction-controlling. The higher C_{VX} is, the longer the induction period becomes, which indicates that the quantity of the VX molecules adsorbed at the surface of TiO₂ is increased. After the induction period finished, the C_{VX} was decreased with obeying the first order reaction. The r_{VX} was plotted in Fig. 3(b) as a function of C_{VX} . The r_{VX} then can be kinetically analyzed by Langmuir–Hinshelwood kinetics as shown in an inset of Fig. 3(b).

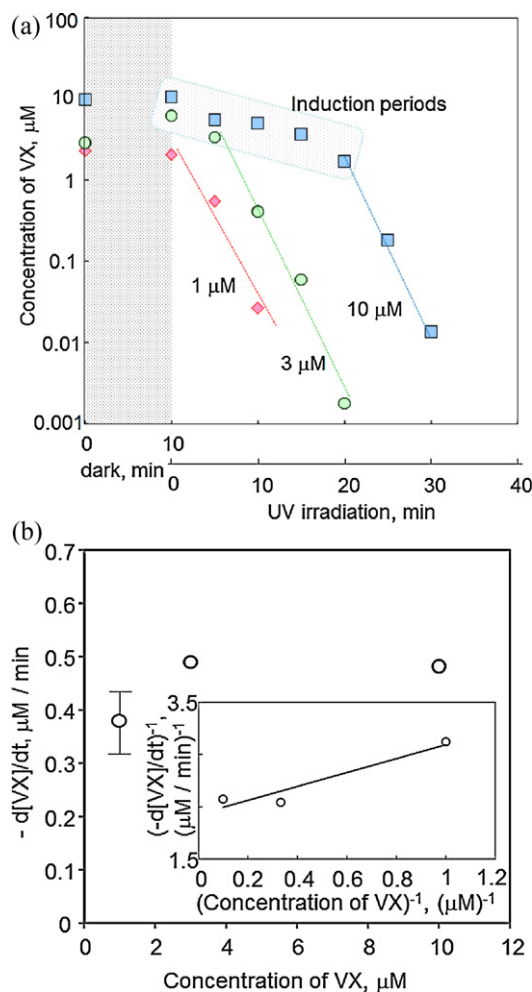


Fig. 3. (a) Concentration of VX dependence on TiO₂ photocatalytic decomposition of VX molecules. The pH of suspension was adjusted to 9 with H₃BO₃–KCl–NaOH buffer and the quantity of TiO₂ powder was 1 g/l. The VX was three different concentrations from 1 to 10 μM. (b) The r_{VX} was plotted as a function of the concentration of VX. The r_{VX} was calculated by first order kinetics equation from (a). The inset was a result of Langmuir–Hinshelwood kinetics analysis.

On the basis of a slope of the inset figure, the r_{max} and K can be calculated by Eq. (1):

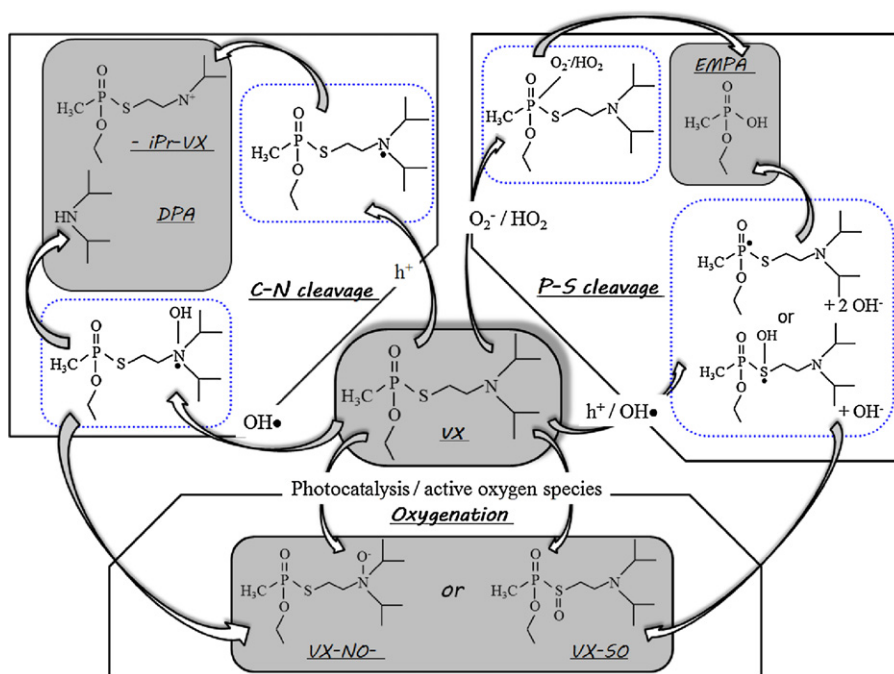
$$\frac{1}{r_{VX}} = \frac{1}{(r_{max} \cdot K) \cdot (C_{VX})} + \frac{1}{r_{max}} \quad (1)$$

Here the r_{max} and K are maximum decomposition rate and adsorption equilibrium of VX molecule and are calculated to be 0.52 μM/min and 2.9 μM⁻¹, respectively, at the TiO₂ photocatalytic decomposition of VX in pH 9 alkaline condition prepared with H₃BO₃–KCl–NaOH buffer.

As mentioned above, since the induction period appears at the high C_{VX} in the TiO₂ photocatalysis, the 1–3 μM is suitable for the experiments to observe TiO₂ photocatalysis in this study.

3.4. Decomposition mechanism speculated from LC–MS/MS analysis

The VX decomposition products were analyzed on LC–MS/MS and the detected products were assigned to diisopropylamine (DPA) as $m/z = 102.13$ of m/z , ethyl methylphosphonic acid (EMPA) as $m/z = 125.04$, oxygenated VX (VX–SO or VX–NO⁻) as $m/z = 284.14$ and partially oxidized VX (–iPr–VX) as $m/z = 226.1$ respectively by reference to mass number and a data base of the equipment. No mass number assigned to EA2192 was detected. Notice that in this



Scheme 3. Plausible TiO_2 photocatalytic decomposition mechanism of VX proposed in the present study.

analysis, the concentration of the by-product could not be identified from the peak intensity of LC–MS/MS analysis because the standard reagent as intermediates observed in this analysis could not be obtained and synthesized. In addition, the detected peak intensity is controlled by the ionization potential of the molecules, so that the comparison of the concentration of each by-product cannot be analyzed by the LC–MS/MS analysis. Accordingly, the TiO_2 photocatalytic reaction mechanism was qualitatively discussed in this study.

The EMPA production is attributable to P–S cleavage as has been known [33,35–37]. The P–S cleavage can be carried out by the reaction with active oxygen species such as superoxide anion (O_2^-), peroxide radical ($\cdot\text{HO}_2$) and hydrogen peroxide (H_2O_2) [35,37,40] which are produced by the TiO_2 photocatalysis [8–13]. In addition, the TiO_2 photocatalytic oxidation by the hydroxyl radical ($\text{OH}\cdot$) and photoinduced hole (h^+) can also carry out the P–S cleavage. The VX-NO^- or VX-SO is then also produced by active oxygen and the VX-NO^- or VX-SO formation is named oxygenation in this study. The VX-SO may be intermediates of EMPA production. The DPA and $-i\text{Pr-VX}$ are produced by the oxidation of: $\text{N}(\text{iPr})_2$ group at the $\text{Ti-N}(\text{iPr})_2$ bond, it is named C–N cleavage in this study. The plausible photocatalytic reaction scheme proposed in this study is shown in Scheme 3.

3.5. Comparison of photocatalytic decomposition rate of VX and DMMP

Fig. 4 shows the decrease of the C_{VX} and C_{DMMP} in the TiO_2 photocatalysis. The quantity of TiO_2 was 1 g/l and the C of VX and DMMP was 3 μM . The r_{VX} was much faster than r_{DMMP} . The r_{VX} and r_{DMMP} were then estimated to be 0.41 and 0.013 $\mu\text{M}/\text{min}$, respectively, that is, the r_{VX} is 30 times faster than r_{DMMP} .

The DMMP molecular structure is similar to VX molecule as shown in Scheme 1. The adsorption structure of DMMP molecule has been known well as $\text{Ti-O=P}(\text{CH}_3)(\text{OCH}_3)\text{-O-Ti}$ bond formation [16,17]. The photocatalytic decomposition of DMMP molecule is then simply carried out by the P–O cleavage only, while the VX molecule is decomposed by the C–N, P–S cleavage and the

oxygenation as suggested in Scheme 2. As seen in Table 1, the E_a of the P–O cleavage of DMMP molecule in alkaline and at the surface of metal oxide is similar to that of the P–S and P–O cleavage of VX molecules. Therefore, the difference of 30 times cannot be simply explained by taking into account the E_a of the P–O and P–S cleavage only. Here, in order to give an understandable explanation, it should be assumed that the E_a of the C–N cleavage and oxygenation at VX decomposition are lower than that of the P–O cleavage of DMMP molecules. In addition, the adsorption quantity of DMMP and VX will be also one of the factors to control r in the TiO_2 photocatalytic decomposition in the alkaline aqueous phase. The larger quantity of VX adsorption can be expected on the basis of the pK_a of VX molecules in alkaline condition but the actual quantity of VX and DMMP

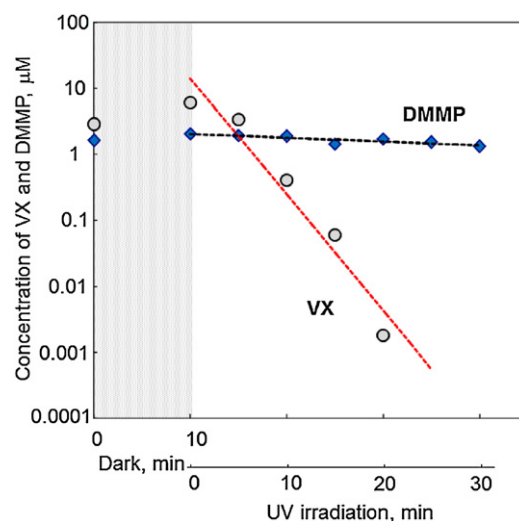
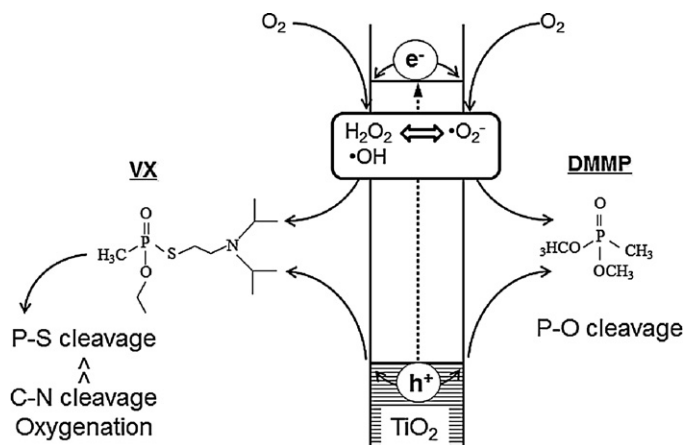


Fig. 4. Photocatalytic decomposition of the VX and DMMP molecules in alkaline aqueous phase. pH was adjusted to 9 with $\text{H}_3\text{BO}_3\text{-KCl-NaOH}$ buffer. The quantity of TiO_2 was 1 g/l and concentration of VX and DMMP were 3 μM .



Scheme 4. Plausible TiO₂ photocatalytic decomposition mechanism of VX and DMMP suggested in this study.

molecules adsorbed at the surface of TiO₂ was unclear in this study (Scheme 4).

3.6. General discussion

The VX molecule was decomposed by the P–S, C–N cleavage and the oxygenation. The P–O cleavage was not carried out by the TiO₂ photocatalysis; no EA2192 was detected. Since the photocatalytic decomposition of VX molecule is carried out at the surface of the TiO₂, the E_a of the functional group of VX structure at the surface of TiO₂ affects the reaction selectivity. The E_a of P–O and P–S cleavage of VX in aqueous phase is calculated to be 60.7 kJ/mol [33]. In contrast, low E_a at the surface of dry silica sand as mainly controlled by P–S cleavage in gas phase is calculated to be 46 kJ/mol [48]. On the other hand, the catalytic reaction at the surface of moist silica sand is mainly controlled by P–O cleavage and the decomposition rate is slowed by adding the moisture. The E_a of P–O cleavage was then calculated to be 80 kJ/mol and was higher than that of P–S cleavage on the dry one and alkaline solution [33,48]. It can be therefore speculated that E_a of P–S cleavage at the surface of TiO₂ in alkaline solution is lower than that of P–O cleavage. The E_a of C–S cleavage is calculated to be 107.5 kJ/mol in alkaline aqueous phase and is higher than that of P–O and P–S cleavage [33], indicating that the C–S cleavage is energetically unfavorable. It is consequently suggested that the TiO₂ photocatalysis may energetically prefer P–S cleavage to P–O cleavage as well as the catalytic reaction of the dry silica sand.

As seen in this study, the VX molecule was quickly decomposed by the TiO₂ photocatalysis in alkaline solution, but the decomposition was partial oxidation of VX molecular structure, not to be complete decomposition as mineralization. The by-products as VX–NO⁻ or VX–SO and –iPr–VX being toxic, the TiO₂ photocatalytic reaction to decompose completely VX molecule needs longer UV irradiation. However, the VX and the by-products will be completely decomposed by the TiO₂ photocatalysis as has been shown in the study on the decomposition of the BAET and DMMP in the TiO₂ photocatalysis [14–30].

4. Summary

The photocatalytic decomposition of VX molecules in aqueous phase was experimentally demonstrated in aqueous phase. The photocatalytic decomposition rate, r_{VX} , became fast with increase in alkalinity. The acceleration of r_{VX} in the alkaline condition was attributable to the increase in the number of decomposition mechanism as a consequence of the increase of the Ti–N(iPr)₂ bond

formation. The several photocatalytic decomposition mechanisms such as the P–S, C–N cleavage and the oxygenation at the surface of TiO₂ photocatalysts were suggested on the basis of LC–MS/MS analysis. One of the benefits of the TiO₂ photocatalytic decomposition of VX was that no EA2192 was produced. In this study, DMMP as a VX simulant was also decomposed by the TiO₂ photocatalysis at the same experimental condition as VX molecule. The r_{VX} was then 30 times faster than r_{DMMP} and the reason could be explained on the assumption that the C–N cleavage and the oxygenation in the TiO₂ photocatalytic decomposition of VX was carried out easier than P–O cleavage of DMMP molecule.

As has been reported by many research groups, the hydrolysis of the VX molecule itself is accelerated in alkaline solution above pH 10 by hydroxyl ion [33–36]. The strong alkaline pH above 10 is also harmful to human-being in the case of actual decontamination in surroundings. As represented in this study, the TiO₂ photocatalysis worked well to decompose VX molecule in pH 7–9 of solution as weaker alkaline condition. The pH from 7 to 9 will be suitable for using safely suspension as decontamination fluid because this pH is similar to seawater and mineral water coming from mountains. These findings give us the reliable information to develop the photocatalytic decontamination systems by using DMMP instead of VX.

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